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POLYMERIZATION OF METALLOCENE-CATALYZED LONG-CHAIN BRANCHED AND FUNCTIONAL POLYPROPYLENE

Doctoral Dissertation

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Abstract

Propylene was polymerized with homogeneous and heterogeneous metallocene catalysts. In addition to homopolymerizations, copolymerizations were conducted with alfa-olefins, dienes and functional comonomers.

Propylene/1,9-decadiene copolymers were polymerized with racemic dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl) zirconium dichloride supported on methylaluminoxane-modified silica. Rheological tests showed long-chain branching in the copolymers, even with comonomer incorporations of less than 1 mol %.

Hydroxyl functional propylene/10-undecen-1-ol copolymers were polymerized with homogeneous racemic dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride. Addition of triisobutylaluminum eliminated the drop in molecular weight with increasing comonomer content, and the interactions between the active center and the hydroxyl group at the end of the comonomer chain were more efficiently blocked. Catalyst activity was improved by increase in the proportion of methylaluminoxane in the cocatalyst mixture. Functionality contents up to 2 mol % were obtained by lowering pressure.

The functional polypropylene exhibited significantly enhanced peel strength and paintability relative to a reference homopolypropylene. Adhesion properties were improved not only in the copolymer but also in a blend consisting of propylene homopolymer and functional polypropylene, even when functionality content was only 0.17 wt %. The functional polypropylene slightly increased the adhesion between polypropylene and polyamide phase or silica filler, although the effect on impact strength was not as good as desired.

In copolymerization with metallocene catalysts, the comonomer distribution is uniform along the polypropylene backbone and the stereospecificity is maintained. The properties of the polypropylene are dramatically affected even with comonomer incorporations less than 1 mol %, regardless of whether the comonomer is a non-conjugated diene to induce long-chain branching or contains a functional group to improve adhesion properties.

Keywords propylene, functional, long-chain branching, adhesion, metallocene, diene, alcohol

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PREFACE

The experimental work for this thesis was carried out between 2000 and 2005 in the Laboratory of Polymer Technology at the Helsinki University of Technology. The projects of which it formed apart were funded by the Academy of Finland, the National Technology Agency of Finland, and Borealis Polymers Oy.

I wish to express my gratitude to Prof. Jukka Seppälä for giving me the opportunity to work in this interesting field. I am indebted to Dr. Barbro Löfgren for her guidance and support.

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Espoo, June 20, 2005.

Santeri Paavola

LIST OF PUBLICATIONS

This thesis is based on the following seven appended publications:

I Uusitalo, A.-M., Pakkanen, T., Kröger-Laukkanen, M., Niinistö, L., Hakala, K., Paavola, S., and Löfgren, B., Heterogenization of racemic ethylenebis(1-indenyl)zirconium dichloride on trimethylaluminum vapor modified silica surface, *J. Mol. Cat. A: Chem.* (2000) **160**(2) 343-356.

II Paavola, S., Saarinen, T., Löfgren, B., and Pitkänen, P., Propylene copolymerization with non-conjugated dienes and α-olefins using supported metallocene catalyst, *Polymer* (2004) **45**(7) 2099-2110.*

III Paavola, S., Uotila, R., Löfgren, B., and Seppälä, J. V., Enhanced adhesive properties of polypropylene through copolymerization with 10-undecen-1-ol, *React. Funct. Polym*. (2004) **61**(1) 53-62.

IV Paavola, S., Löfgren, B., and Seppälä, J. V, Polymerization of hydroxyl functional polypropylene by metallocene catalysis, *Eur. Polym. J.* (2005) **41**(12) 2861-2866.

V Hippi, U., Korhonen, M., Paavola, S., and Seppälä, J., Compatibilization of poly(propylene)/polyamide 6 blends with functionalized poly(propylene)s prepared with metallocene catalyst, *Macromol. Mater. Eng.* (2004) **289**(8) 714-721.

VI Ristolainen, N., Vainio, U., Paavola, S., Torkkeli, M., Serimaa, R., and Seppälä, J., Polypropylene/organoclay nanocomposites compatibilized with hydroxyl-functional polypropylenes, *J. Polym. Sci. Part B: Polym. Phys.* (2005) **43**(14) 1892-1903.

VII Uotila, R., Hippi, U., Paavola, S., and Seppälä, J., Compatibilization of PP/elastomer/microsilica composites with functionalized polyolefins: effect on microstructure and mechanical properties, *Polymer* (2005) **46**(19) 7923-7930.

* An invention disclosure has been made to Borealis Polymers Oy and they have claimed all rights concerning the method described in publication **II**.

My contribution to the appended publications was as follows:

Publication I: I carried out a major part of the polymerization and polymer characterization and wrote the corresponding part of the manuscript with the co-authors.

Publication II-IV: I planned the experiments, carried out the polymerization and characterization of polymers, and wrote the manuscript together with the co-authors.

Publication V-VII: I carried out the polymerization and characterization of the polymers and assisted in the preparation of the manuscript.

POLYMERIZATION OF METALLOCENE-CATALYZED LONG-CHAIN BRANCHED AND FUNCTIONAL POLYPROPYLENE

CONTENTS

ABBREVIATIONS

Al/Zr	aluminum/zirconium ratio
Cp	cyclopentadienyl
Cl	chloride
DD	1,9-decadiene
DEAC	diethylaluminum chloride
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
EAC	ethylaluminum chloride
EPS	expanded polystyrene foam
Et	ethyl
Flu	fluorenyl
FTIR	Fourier transfer infrared spectroscopy
GPC	gel permeation chromatography
HDPE	high density polyethylene
Hx	1-hexene
Ind	indenyl group
i-Pr	*iso*-propyl
LDPE	low density polyethylene
MAH	maleic acid anhydride
MALLS	multi-angle laser light scattering
MAO	methylaluminoxane
Me	methyl
MOD	7-methyl-1,6-octadiene
mol %	mole percent
MWD	molecular weight distribution
NMR	nuclear magnetic resonance spectroscopy
PA	polyamide
PE	polyethylene
Ph	phenyl
$[PhNMe_2H]^+[B(C_6F_5)_4]^-$	dimethylanilinetetrakispentafluoroborate

PP	polypropylene
PP-g-AA	acrylic acid grafted polypropylene
PP-g-MAH	maleic anhydride grafted polypropylene
PS	polystyrene
PVC	polyvinylchloride
SAXS	short angle X-ray scattering
SEM	scanning electron microscopy
TEA	triethylaluminum
TIBA	triisobutylaluminum
TMA	trimethylaluminum
wt %	weight percent
Zr	zirconium
14C	1-tetradecene

SYMBOLS

E_a	Arrhenius-type flow activation energy (kJ/mol) determined by Arrhenius equation: $\eta = A \times e^{\frac{E_a}{RT}}$, where η is viscosity, A a constant, e Eulers number, R universal gas constant and T temperature
G'	storage modulus (Pa)
G"	loss modulus (Pa)
ΔH_m	melting enthalphy (J/g)
$\overline{M_n}$	number average molecular weight (kg/mol)
$\overline{M_w}$	weight average molecular weight (kg/mol)
$\overline{M_w} / \overline{M_n}$	molecular weight distribution
η_0	zero shear viscosity (Pa × s)
T_m	melt temperature (°C)

1 INTRODUCTION

Polypropylene is the most versatile of the commodity polymers being produced in large volumes from inexpensive raw materials. It has numerous favorable properties, including low density, good thermal behavior, appropriate processability, and relatively high chemical and corrosion resistance. Additionally, its mechanical properties are close to those of engineering thermoplastics, and the difference can be diminished with use of fillers and reinforcements. High material and processing costs plague many composites based on thermoplastics, and in this respect polypropylene offers cost benefits as well. Polypropylene is also superior from the environmental point of view. The main end uses of polypropylene are in injection molding, fiber, film, and extrusion. (Fig. 1)

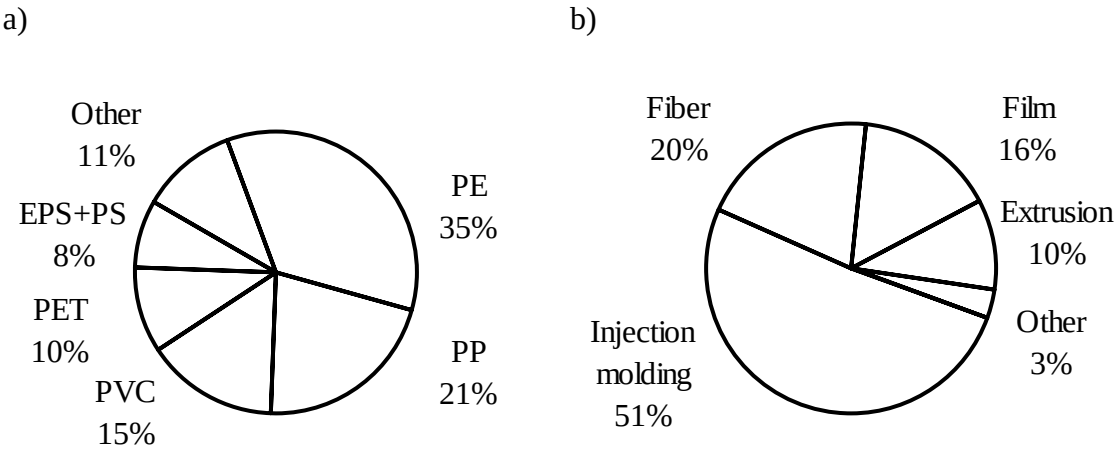

Figure 1. Consumption of plastics in Western Europe[1] a) and of PP in different applications b)[2].

2 HETEROGENEOUS CATALYSTS

Homogeneous metallocene catalysts can be successfully applied in some solution processes, but for wider industrial use a heterogeneous catalyst is required. In continuous slurry processes, fluidized-bed gas-phase processes, and bulk polymerization processes, the polymer is insoluble in the reaction medium and a morphologically uniform polymer product would be advantageous in decreasing reactor fouling. One way to obtain good morphology and to reduce reactor fouling is to immobilize the normally soluble metallocene on a carrier. Reported and patented support materials include silica and other inorganic oxides, metal halides, polymers, metals, ceramics, celluloses, starches, and clays.[3]

There are high expectations for heterogeneous metallocene catalysts. The polymerization process is expected to deliver higher productivity and to be more controlled. Since the cost of the metallocene catalyst system depends more on the methylaluminoxane (MAO) cocatalyst than the catalyst itself, it is hoped that metallocenes supported on modified carriers will be active without the need for external MAO. If this proves too demanding, a decrease in the aluminum to zirconium ratio or in the absolute concentration of MAO might be sufficient. Another excellent result would be the replacement of MAO totally or partially with a common aluminum alkyl such as trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA), diethylaluminum chloride or ethylalumium chloride, or with more exotic boron compounds. Desired improvements in the properties of the polymer are good morphology, more controlled molecular weight distribution, e.g. from narrow to bimodal, and high molecular weight.[4]

2.1 Silica support

Silica is the most widely examined carrier material for metallocenes. The first patents were obtained by Hoechst in 1990.[5] Relatively high activities can be achieved if the silica is porous enough to give access to the large metallocene molecules. Also important are mechanical strength, stability, and sintering of the silica support.

There are several different methods to immobilize metallocene on the support surface: 1) adsorption of metallocene directly on the support without additional aluminum alkyl, 2) adsorption of MAO, TMA, or TIBA on silica, and addition of metallocene in the second step, 3) adsorption of the metallocene followed by treatment with a suitable aluminum alkyl.[6]

Porosity, pore size, and specific surface area affect the ability of the silica to react with the metallocene. For their part, chemical surface properties can be modified by removing water from the silica by preheating; the silica is partially dehydroxylated and the number of the free hydroxyl groups available for reaction is reduced. A more stable support is obtained when the calcination temperature is over 500 °C.[7, 8]

Aluminum alkyl behaves as cocatalyst and activates the metallocene, and it is an excellent scavenger of impurities. Aluminum alkyl treatment of the silica support stabilizes the support, but only at low calcination temperature of 200 °C. When enough water is removed at 400 °C-800 °C, MAO treatment only hinders the reaction between scarce hydroxyl groups and metallocene and adsorption of the catalyst.[9]

2.2 Binary catalysts

Two polymerization processes can be combined when two different types of metallocenes are immobilized on the same carrier. Przybyla *et al.*[10] were able to immobilize an isotactic working species (*rac*-$Me_2SiInd_2ZrCl_2$) and a syndiotactic working species (*i*-$PrFluCpZrCl_2$) on the same MAO-modified silica obtained from the PQ-corporation. With TEA as cocatalyst, a stereoblock polypropylene with controlled isotactic and syndiotactic blocks was obtained. A simultaneous adsorption and homogeneous distribution of the two metallocenes is essential to the success.

2.3 Activation with common aluminum alkyls

Because of the high cost of MAO, it would be economically beneficial to replace it with cheaper compounds, for example with common aluminum alkyls. Arrowsmith *et al.*[11] have reported propylene polymerizations with *rac*-Me_2Si(2-Me-4-1-naphthyl-Ind)$_2ZrCl_2$/MAO supported on silica coactivated with TIBA alone. Polymerizations were performed in bulk, in toluene slurry, in a stirred NaCl bed, and in a stirred polyethylene bed. Weiss *et al.*[12] examined basic *rac*-Et(Ind)$_2ZrCl_2$ supported on clay pretreated with TMA or TIBA. No external MAO was needed to active the catalyst but TMA or TIBA was sufficient as cocatalyst.

Soga and his research group[13, 14, 15] were successful in preparing various catalyst systems that could be activated with common aluminum alkyls. Zirconocenes as well as titanocenes were tested, while the support materials included magnesium dichloride and aluminum trioxide. No external MAO was added which ensured that no leaching occurred. The inorganic support material was pretreated only with TMA or TEA, and in

the polymerization, TMA, TEA or TIBA was sufficient to activate the catalyst. The isotacticity of polypropylene could be influenced by a proper choice of reagents, use of ethylbenzoate or boron compounds, for example, increased the isotacticity.

2.4 Polymeric carriers

Although inorganic support materials are widely used, they suffer from several drawbacks. Most notably, inorganic residues in the polymer product weaken the mechanical properties and may affect the clarity. The phase separation is less pronounced with polymers as carrier materials. Natural polymers[16] have been employed, but synthetic polymers are more common.

Chukanova *et al.*[17] grafted acrylic acid on polyethylene and used this as support material in propylene polymerization. The carrier was modified with MAO or with both MAO and borate before impregnation. The metallocene was *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$, which is characterized by its high isospecificity and polymerization activity. The supported catalyst could be activated with TIBA, and no additional MAO was needed. Loss of isotacticity due to immobilization could be diminished by borate treatment of the support.

Soga‘s group[18, 19] studied polysiloxane as a support material for zirconocene. Because of the low molecular weight of the polysiloxane, the support material was partially soluble in the MAO/toluene mixture and the heterogenization was not complete. Besides the dominant syndiotactic blocks, atactic and isotactic blocks were present in the polypropylene product. The solubility of the support was also problematic with the silylphenyl chains.[20]

Soga and his research group[21] also examined a catalyst supported on polystyrene, where the catalyst was synthesized directly on the support. Styrene containing the 1-Cp-1-FluEt ligand was polymerized with ordinary styrene, and then zirconium tetrachloride was allowed to react with the cyclopentadienyl and fluorenyl ligands. Zirconium tetrachloride reacted with ligands attached to the same molecule but also with ligands attached to separate polystyrene chains, so linking them together. The low molecular weight fraction was soluble in toluene, but possibly due to cross-linking by zirconocene, part of the catalyst was heterogeneous. Even though homogeneous *i*-$PrCpFluZrCl_2$ should be syndiospecific, and on a silica support isospecific, complexity of the catalyst synthesis meant that many different active species were present and the polypropylene had isotactic, atactic, and syndiotactic blocks

Roscoe *et al.*[22] took a different approach, in which the metallocene was not covalently bonded to the support but ionic interactions were involved. The benefits are the flexibility of the catalyst synthesis, i.e., the metallocene can be varied and the method is useful, for example, in catalyst screening. The polystyrene used as the support was first cross-linked with divinylbenzene, then chloromethylated and treated with a secondary amine. In the next step, $[PhNMe_2H]^+[B(C_6F_6)_4]^-$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrMe_2$ were attached to the amine groups of the support by ionic interactions. The method can be modified by varying the cross-linking degree, particle size, and functionalization level of the support, as well as the chemistry involved in the active catalyst formation. The catalyst was heterogeneous because propylene was polymerized in bulk rather than in organic solvents. Microstructure and morphology of the polypropylene were not as uniform as was expected.

3 FUNCTIONAL POLYPROPYLENE

Polypropylene suffers from poor adhesion properties and incompatibility with technical plastics, aluminum, steel, and glass. The lack of reactive groups significantly limits the areas in which it can be applied. Because of the otherwise good properties of polypropylene, its functionalization has attracted great interest of late.[23]

The most beneficial type of compatibilizer for polymer blends might be a diblock copolymer, where the polypropylene chain end would penetrate into the polypropylene phase and the polar chain end into the other phase. Diblock copolymers can be obtained by exploitation of chain end unsaturations[24, 25, 26, 27] or by using styrenic[28] or aluminum-based[29] chain transfer agents. The end groups can be converted into various functional groups through post-modification. The functional group at the end of the polypropylene chain acts as a starting point for the growth of methylmethacrylate,[24] caprolactone,[26, 28] or propylene glycol[30] chains in atomic transfer radical polymerization or in other polymerization techniques. But since post-treatment is performed in several stages, it is time-consuming and costly.

A statistical comonomer distribution might be sufficient in polymer composites and in adhesion applications to metal but in the key applications, where paintability, printability, and affinity for dyes are needed, a uniform comonomer distribution is essential. With metallocene catalysts the comonomer reacts in a controlled manner and a uniform comonomer distribution is obtained.

The traditional functional material has been maleic acid anhydride (MAH), which is grafted directly on polypropylene. The comonomer distribution is purely statistical and the polypropylene is liable to cross-linking, chain-scission, and severe degradation, although the latter can be slightly diminished by using vinyl acetate in

combination with MAH.[31] Despite the statistical comonomer distribution, at least with irradiation induced graft reactions, the wettability of polypropylene is improved. And with the right choice of reagent, the smoothness of the polypropylene thin film surface is preserved.[32]

3.1 Direct copolymerization

In general, the polymerization of monomers containing functional groups with Ziegler-Natta catalysts is limited by the intolerance of the catalysts to Lewis bases, which leads to catalyst deactivation, polymer degradation, and comonomer homopolymerization. Nevertheless, there are some patents in this area even with the reduced activity of the Ziegler-Natta catalyst.[33, 34]

If it is impossible to find a catalyst that tolerates oxygen or, for example, less reactive acrylate salts, there are several methods to fight against catalyst deactivation. Reactivity of the functional group can be diminished by reducing its electron-donating ability or by protection chemistry, i.e. by changing hydroxyl groups into trimethylsiloxy or alkoxy groups. Reactive functional groups and double bonds can also be insulated from each other with a spacer or by creating steric hindrance around the functional group. In practice, two or more of the above-mentioned methods are combined to achieve satisfactory results.[35]

Metallocene-based catalysts offer a way to polymerize alcohol functional comonomers with propylene, but even then the catalyst activity is on a much lower level than in homopolymerization. The comonomer forms a stable complex with the catalyst and prevents the formation of a π-complex between the catalyst and double bond of the incoming monomer, or it interacts with the electric forces and hinders the formation of

the π-complex, although allowing the polymerization reaction to continue with somewhat lower activity. The catalyst is not totally poisoned, however, and the stereospecificity as well as uniform comonomer distribution are maintained.[35]

With metallocenes as catalyst, a wide variety of monomers can be copolymerized with propylene. Aside from the most researched long linear α-olefin alcohol,[36] also carboxylic acid, ester,[37] amide,[38] amine,[39] and methyl acrylate[40] can be copolymerized with propylene. Hakala *et al.*[37, 38] examined the effect of bulky substituents, spacer length, and type of functionality on the catalyst activity. Alcohol was found to be more reactive than acid or ester, and ketone strongly deactivated the catalyst. A long spacer between polymerizable double bond and the oxygen favored the copolymerizability of the functional comonomer. Also, steric protection around the functional group diminished catalyst deactivation, though not to the same degree as the long spacer.[37] Functionalized polypropylenes exhibited good peel strength towards aluminum, whereas the homopolymer had none.[35] According to contact angle measurements with water, hydrophilicity increased as desired.[41]

Some more exotic catalysts have been tested. For example, palladium-based catalyst copolymerized methyl acrylate[42] and even carbon monoxide, a common catalyst poison.[43, 44] With methyl acrylate, a highly branched amorphous polymer with no stereostructure was obtained, but with carbon monoxide the copolymer was claimed to have uniform and alternating comonomer distribution and isotactic structure.

An oxygen tolerant catalyst might also be found amongst exotic rare earth metal based catalysts, which have been reported to copolymerize some longer α-olefins with caprolactone[45, 46] and methylmethacrylate.[46] The cocatalyst could play an important role, and the use of boron compounds as cocatalyst might prove successful.[47] The use of

different aluminum alkyls in combination could result in an alkyl group exchange and new cocatalyst compounds.[41, 48, 49, 50]

Tolerance towards comonomers containing heteroatoms can be improved by trapping the heteroatom inside a cube. A cycloalkene-substituted alkoxyamine[51, 52] and a monomer containing a silsesquioxane cage[53] have been polymerized with propylene using zirconium and titanium based metallocenes. Because the heteroatom is trapped in a cage and isolated from outside interactions, other properties than improved surface adhesion are sought with these comonomers. Siloxane could improve scratch and thermal resistance if used in large proportions, and amine compounds could act as light and thermooxidative stabilizers. Amines also act as initiating groups for living polymerization and could lead to new graft polymers.

Barbosa *et al.*[54] used a totally different approach to adhere polypropylene onto glass fiber. First the preheated glass fiber monofilaments were treated with MAO to obtain Al_2O_3 onto the glass fiber surface. TMA was tested, too, but it proved ineffective. The propylene and long linear α-olefin alcohol were then copolymerized directly on the glass fibers. Part of the copolymer was chemically bonded to the glass fibers. Such bonded copolymers could find use in glass fiber thermoplastic composites with improved fiber-matrix adhesion.

3.2 Post-modification of unsaturations

The unsaturations present in polypropylene, e.g. vinylidene end group through β-H transfer, vinyl through β-CH_3 transfer, and isobutenyl, can be exploited and freely converted into various functional end groups.[55] The functionalities include anhydride, silane, thiol, epoxy, borane, and carboxylic acid. Depending on the functionality

desired, the polypropylene is exposed to harsh treatment, from a few hours in solvent at mild temperatures to 24 hours in boiling hot acidic solution. Shiono and his group[56] were able to convert aluminum-terminated polypropylene into hydroxyl functional end group simply by bubbling it with oxygen gas. Functionality content of 0.12 mol % could be doubled by increasing the reaction time and heating from room temperature to 120 °C.

A more sophisticated method is to copolymerize non-conjugated dienes with propylene using a metallocene catalyst, as then the double bonds are evenly divided along the backbone in side chain ends. To avoid reaction of both double bonds, the dienes are often asymmetric and there is some kind of steric hindrance around the other double bond.

The method was patented for Ziegler-Natta catalyst in 1989 by Mitsubishi.[57] The patent offered several different chemical routes to convert a double bond into hydroxyl or epoxy functionality. The end product had increased adhesion properties towards polyamide. Also an improved adhesion to steel has been reported for this kind of system.[58] Hackmann *et al.*[59] used the metallocene catalyst *rac*-Et$(Ind)_2ZrCl_2$ in the copolymerization of several non-conjugated dienes with propylene and converted the free double bonds in the copolymer into epoxy functionality by 3-chloroperoxybenzoic acid treatment.

Song *et al.*[60] exploited the idea further and used ozonolysis to convert double bonds of 7-methyl-1,6-octadiene into aldehyde functionality, which can then be converted into carboxylic acid, ester, or nitrogen based functionalities. A reaction route from unsaturation first to aldehyde and then to carboxylic acid leads to acid chloride,

which reacts eagerly with colorants. These dye-carrying polypropylene fibers had high color intensity and could be blended into propylene homopolymer.

Arnold *et al.*[61] reported that titanocene-based catalysts might also favor the linear addition of symmetric dienes. Then the free double bond left in the polymer would be more reactive because of the absence of steric hindrance. Epoxy functionality was obtained with post-modification, and the ring could be opened to form two hydroxyl groups.

3.3 Precursors as a source for functionalities

A reactive functional group in the comonomer can be protected. Hydroxyl, for example, can be converted into siloxy or alkoxy groups for the duration of polymerization, and converted back to its original functionality after the polymerization. A slightly different approach is to use totally different precursors, which do not deactivate the catalyst during polymerization and which after polymerization can be converted into functional groups with chemical modification.

Chung *et al.*[25] investigated borane-containing comonomers in propylene copolymerizations. These have more often been used as initiators for acrylate or caprolactone[26] grafting reactions, but the borane group can easily be converted to hydroxyl functionality through sodium hydroxide treatment followed by hydrogen peroxide treatment. Borane-containing comonomers are better tolerated, by both Ziegler-Natta and metallocene catalysts, than are polar functional monomers.

4 LONG-CHAIN BRANCHING IN POLYPROPYLENE

A key feature of metallocene-catalyzed polymer is the narrow molecular weight distribution, which then is associated with a narrow processing window due to poor shear thinning.[62] Long-chain branching improves the processability of polypropylene. An improved melt strength enables new possibilities in blow molding, foaming, thermoforming, fiber spinning and extrusion coating. In addition, wall thickness can be reduced resulting in lower material consumption.

The simplest method to improve processability is to make a blend of polypropylene with desired properties and low-density polyethylene with good processability, but typically all the good properties of polypropylene are lost in the mixing, especially the film transparency, film strength and heat resistance.[63, 64]

Three main routes to long-chain branched polypropylene discussed as follows are connecting chains together with dienes and silanes, copolymerization with previously prepared macromonomers and cross-linkage with irradiation and peroxides.

4.1 Dienes and silanes

Dienes have two double bonds, both of which can react with the growing polypropylene chain. (Fig. 2) As a result, an H-shaped branched polypropylene may be formed. Exxon[65] patented the diene method for Ziegler-Natta catalyst in 1996. Aside from linear dienes, also branched and cyclic dienes can be used. The propylene copolymer was crystalline, gel-free, and long-chain branched without cross-linking.

The use of metallocene catalysts *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ and *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ for propylene copolymerization with 1,7-octadiene,[66, 67]

1,9-decadiene[66, 67, II] and branched 7-methyl-1,6-octadiene[67, II] has been reported for the same purpose.

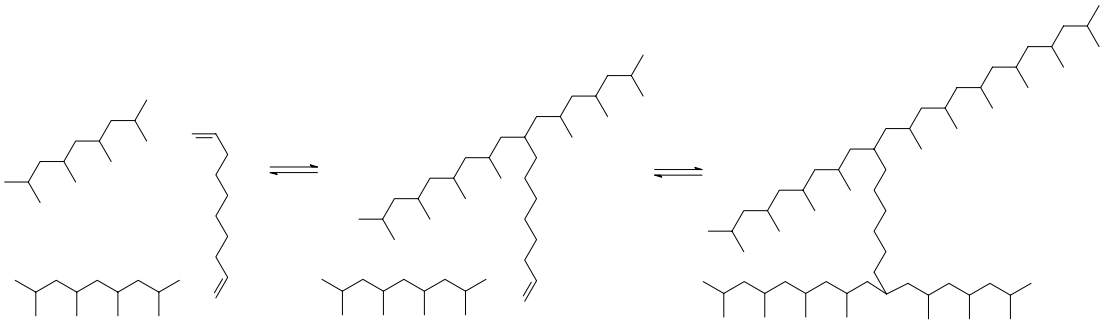

Figure 2. The formation of long-chain branching through reaction with a diene.[II]

Nextrom[68, 69] has patented a method where silanes were used in a slightly different manner as a cross-linking agent. First polypropylene was grafted with silane and then it was cross-linked by using water and dibutyltindilaurate to initiate a reaction between the silane side groups. The use of corrosive silane compounds and peroxides can be eliminated from the extrusion process by grafting the silane to the polypropylene prior to extrusion.

4.2 Macromonomers

Weng *et al.* [70, 71, 72] have performed a thorough study on the use of vinyl-rich polyethylenes and polypropylenes as macromonomers. With use of previously prepared macromonomers, all long-chain branches in the polypropylene were equally long and the chain length can be controlled. A high vinyl content, i.e. polymerizable double bonds, is crucial to the copolymerization of macromonomer with propylene.

Metallocene catalyst *rac*-Me_2Si(2-Me-4-Ph-1-Ind)$_2ZrCl_2$ polymerized propylene with high vinyl chain-end selectivity at elevated temperatures.[73]

The use of polyethylene as macromonomer in propylene polymerizations has also been reported, but the product is a crystalline copolymer of propylene and ethylene and not long-chain branched pure polypropylene.[74, 75] The properties of the polypropylene might be affected by the polyethylene content. Uniformity is also lost if the monomers differ significantly from each other, in stereostructure for example. This applies to the use of atactic polypropylene as long-chain branches in highly isotactic polypropylene.[76]

The reaction route to long-chain branched polypropylene is quite long if the macromonomer has to be produced and analyzed first, and then be used in the copolymerization in second step. The reaction is faster if different catalysts are used in the macromonomer homopolymerization and the copolymerization. A combination of a bisiminepyridine iron catalyst and a silyl-bridged zirconocene has been successfully applied in polymerizing atactic polypropylene chains and then polymerizing these with propylene to produce long-chain branched polypropylene. The catalysts have to be added stepwise because when they are added simultaneously only two homopolymers are obtained.[77]

4.3 Peroxides and irradiation

Long-chain branches can be induced in polypropylene by cross-linking by chemical means or by irradiation. Montell[78] has patented a method where commercial polypropylene is irradiated in the presence of a controlled amount of oxygen.

Lagendijk *et al.*[79] applied several peroxycarbonates with different chain lengths successfully to modify commercial polypropylenes during extrusion. More complex peroxydicarbonate compounds, i.e. with long or bulky side groups, favored branching in polypropylene, whereas *t*-butylperoxy neodecanoate (Perester) caused only chain-scission and decrease in molecular weight. The degree of long-chain branching could be controlled by the type and concentration of the peroxydicarbonate.

Branching can be further increased by irradiating the peroxy-treated polypropylene, but this occurs at the expense of molecular weight distribution, which is broadened due to the cross-linking of polypropylene chains during irradiation.[80] Himont[81] has patented a method involving irradiation in the presence of non-conjugated dienes to produce long-chain branching in polypropylene.

Although use of ionizing radiation may lead to improved processability, it causes chain-scission and polymer degradation where the uniformity is lost, and also the good properties of polypropylene are affected.

4.4 Determination of long-chain branching

High-resolution ^{13}C NMR is an excellent aid in characterizing polymer structure. Although it cannot detect a difference between a side chain of six carbon atoms and a long-chain branch, it can support data obtainded from other analytical methods.

If a suitable solvent and high temperatures can be employed, GPC-MALLS easily detects long-chain branching can be easily determined from the smaller radius of gyration. Linear standards are crucial.[72]

Because of the cost of high-resolution NMR and high-temperature GPC-MALLS, long-chain branching is most often determined by dynamic rheological method. Compliance, extensional viscosity, zero shear viscosity, modulus, and flow activation energy are all in some degree affected by long-chain branching.

Long-chain branching increases strain hardening, which is manifested as increase in extensional viscosity. The effect is more pronounced at high strain where the viscosity curve turns sharply upwards when branching is increased.[79] The zero shear viscosity is mainly dependent on the molecular weight, but also on the broadening of molecular weight distribution,[82, 83] high molecular weight tail, cross-linking and long-chain branching, all of which increase the zero shear viscosity. The viscosity curve becomes more linear and the plateau at low shear rates becomes more difficult to detect and finally disappears as branching is increased.[84] The effect of branching on viscosity is depicted in figure 3.

a) b)

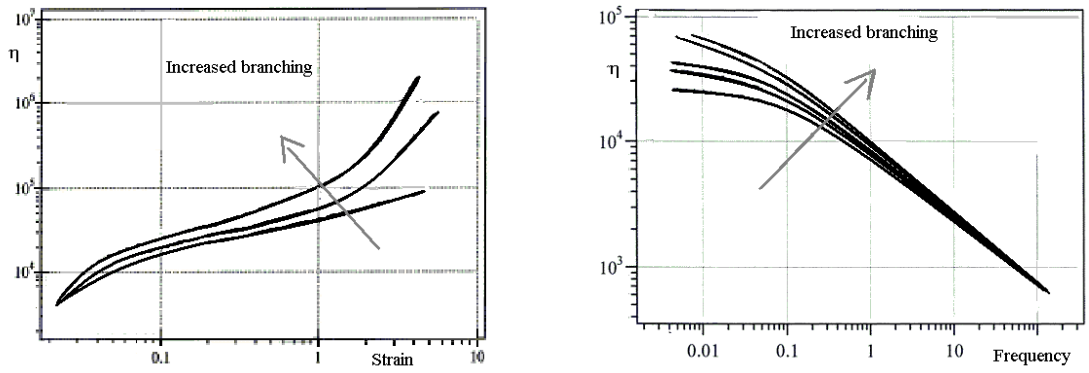

Figure 3. Effect of branching on a) extensional and b) complex viscosity.

Long-chain branching increases shear thinning, but so does broad molecular weight distribution, and the two causes may be difficult to distinguish.[85] Strong and

sharp shear thinning behavior, increase in the contribution of storage modulus, and early crossover of the moduli at low frequency suggest cross-linking or long-chain branching.

In linear isotactic polypropylenes, the Arrhenius-type flow activation energies E_a vary from 27 kJ/mol to 40 kJ/mol. [86, 87, 88] For isotactic polypropylene with molecular weight distributions ranging from 5 to 10, E_a has been reported to be 42-43 kJ/mol,[89, 90] which means that E_a is independent of molecular weight distribution. The E_a value of 51 kJ/mol reported for syndiotactic linear polypropylene is slightly higher.[88] With long-chain branched polypropylene where branches were induced by electron beam treatment, the E_a was 55 kJ/mol, which is significantly higher than with linear polypropylene.[91] The presence of long-chain branching thus appears as a clear increase in the Arrhenius-type flow activation energy.

5 SCOPE OF THE WORK

In the Laboratory of Polymer Technology metallocenes have been of great interest for the last ten years. Their ability to polymerize numerous different monomers has been widely exploited. Although the main focus has been on producing long-chain branched or functional polyethylene and in using this as a compatibilizer in polyethylene blends, study has also been made of polypropylene.

The present document summarizes the research reported in the seven appended publications (**I-VII**). The purpose of the research was to apply metallocenes in olefin homo- and copolymerizations and evaluate the value that they bring in unique properties of polypropylene.

First, two supported metallocene catalysts were used in propylene polymerization (**I**, **II**). Propylene was copolymerized with non-conjugated dienes and the long-chain branching in the copolymers was verified with dynamic rheometer (**II**). Then propylene was copolymerized with straight long-chain alcohol to introduce polar groups to the polypropylene backbone while maintaining the excellent properties of polypropylene (**III**, **IV**). Optimal cocatalyst, comonomer, and monomer concentrations were sought for maximal polymerization activity and comonomer incorporation. Also, the effects of comonomer type and composition were evaluated.

Finally, these functional polypropylenes were used in several applications requiring improved adhesion properties. Surface adhesion properties such as contact angle with water, adhesion to aluminum, and paintability were tested (**III**). One of the goals was to eliminate the use of maleic acid anhydride, a hazardous compound, by finding a new adhesion promoter for polypropylene/polyamide (PP/PA) blends (**V**) and polypropylene/silica composites (**VI**, **VII**).

6 POLYMERIZATION PROCEDURE

All materials used in the polymerization were purified to remove typical catalyst poisons such as oxygen, carbon dioxide, and water. Toluene and *n*-heptane were purified by circulating them through 3-Å molecular sieves, BASF R3-11 copper catalyst, and activated Al_2O_3 columns. Propylene was purified by conducting it through columns containing 3-Å molecular sieves, BASF R3-11 copper catalyst, and activated Al_2O_3. The catalyst solutions were prepared in a glove box. The comonomers were dried with molecular sieves.

The polymerization experiments were carried out in a 0.5 dm^3 stainless steel autoclave reactor equipped with a propeller-like stirrer. The reactor was evacuated and flushed with nitrogen several times before the addition of the polymerization medium (toluene or *n*-heptane). The total volume of the polymerization medium was 300 cm^3. Polymerization temperature was controlled by circulating water in the reactor jacket. Partial pressure of the monomer was maintained constant with an electronic pressure controller. Propylene consumption was monitored during polymerization. The polymerization was stopped by cutting off the propylene feed. The reactor was degassed, and the polymer was precipitated with a mixture of ethanol and a small amount of concentrated hydrochloric acid. The product was isolated by filtering, then washed with ethanol and *n*-pentane or acetone, and dried in vacuum at 40 °C.

With homogeneous catalysts, the reactor was saturated with propylene and then the polymerization was initiated by introducing the toluene solution with dissolved metallocene by means of a dosing pump. In copolymerizations with 10-undecen-1-ol, the comonomer was added with a syringe after toluene and cocatalyst, and the mixture

was stirred for 15 minutes to allow the possible formation of complexes between comonomer and aluminum alkyl.

With heterogeneous catalysts, a suspension of the catalyst in the polymerization medium was prepared in a glove box and introduced to the reactor with nitrogen pressure. The polymerization was initiated by introducing propylene. In copolymerizations with 1,9-decadiene and 7-methyl-1,6-octadiene, the comonomer was added batchwise with a dosing pump at the beginning of the polymerization.

7 POLYMER CHARACTERIZATION

The molecular weights ($\overline{M_w}$) and molecular weight distributions ($\overline{M_w}/\overline{M_n}$) of the polymers were determined with a Waters 150-C ALC/GPC gel permeation chromatograph operating at 140 °C and equipped with Waters Styragel HMW columns and a refractive index detector. The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of 1.0 cm^3/min. The columns were calibrated with narrow molecular weight distribution polystyrene standards using a universal calibration method.

Melting temperatures (T_m) and enthalpies (ΔH_m) were determined with a Mettler Toledo DSC 821^e differential scanning calorimeter. Indium was used for the calibration of the temperature scale. The melting endotherms were measured upon reheating of the polymer sample to 190 °C (160 °) at a heating rate of 10 °C/min.

The ^1H and ^{13}C NMR spectra of polypropylenes were recorded on a Varian Gemini 2000 300 MHz spectrometer. The ^1H NMR samples were dissolved in deuterated 1,1,2,2-tetrachloroethane-d_2 and the residual solvent resonance was used as an internal reference and assigned the chemical shift δ 5.91 ppm. The ^{13}C NMR samples were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (90/10 w/w), and the [mmmm] methyl signal of polypropylene was used as an internal reference and assigned the chemical shift δ 21.8 ppm.

Rheological analyses were performed on a Rheometric Scientific SR-500 stress-controlled dynamic rheometer. Frequency sweeps were carried out at three different temperatures under nitrogen atmosphere. A 25-mm plate-plate geometry and a 1-mm sample gap were used for stiff materials, a 25 mm cone-plate geometry and a 0.045 mm sample gap otherwise. The angular frequency was from 0.01 to 100 rad/s.

Frequency sweep measurements were carried out within the linear viscoelasticity region, which was ensured by a stress sweep. The thermal stability of selected samples was examined with a time sweep. Thermal stability throughout the rheological testing was checked by repeating one low-frequency measurement point (ω = 0.02 rad/s) after the primary frequency sweep. In all samples, the change in storage modulus G' during the frequency sweep was less than 5%. To prevent degradation during measurement, 2000 ppm Irganox B215 antioxidant (Ciba-Geigy, Basel, Switzerland) and 500 ppm calcium stearate were added. Rheometrics RSI Orchestrator software version V6.5.3 was used to extrapolate zero shear viscosities using the Ellis model fit method and to shift the moduli curves along the frequency axis to construct the master curves and determine the shift factor a_T. The shift factors were then plotted against 1/T to obtain the Arrhenius-type flow activation energy E_a. Only E_a values from time-temperature superposition measurements with correlation coefficient of 0.99 or higher were acceptable.

FTIR spectra were measured with a Nicolet Magna FTIR spectrometer 750 from melt-pressed polymer sample films. Ash contents were measured by burning away the organic part in the polymer samples during 60 minutes in a muffle oven at 600 °C. A CAM 200-Optical Surface Tension/Contact Angle Meter (KSV Instruments) was used for the contact angle measurements.

Compounding and blending were done in a co-rotating twin-screw midi-extruder (DSM, capacity 16 cm^3, screw length 150 mm) with a screw speed of 65 rpm. After mixing, specimens for tensile, impact, and dynamic mechanical analysis were injection-molded using a mini-injection molding machine (DSM).

The phase structure of the blends and composites was examined with a JEOL JSM-6330F field emission scanning electron microscope (FESEM). Tensile properties and T-peel strength were characterized using an Instron 4204 universal testing machine operating at a test speed of 2 mm/min. The tensile tests were conducted according to standard ISO 527-1993(E) using specimen type 1BA. T-peel strengths were measured from table pressed plates according to the standard ISO 11339:1993 (E). Surfaces of the aluminum sheets were cleaned with acetone before processing. Charpy impact strength tests of notched specimens with dimensions 4 x 6 x 50 mm were carried out according to standard ISO 179-1993 (E) using a Zwick 5102 pendulum-type testing machine. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer DMA-7 using three-point-bending geometry.

8 RESULTS AND DISCUSSION

The two metallocenes examined were racemic ethylene*bis*(1-indenyl)zirconium dichloride (*rac*-Et(Ind)$_2$ZrCl$_2$) and racemic dimethylsilanyl*bis*(2-methyl-4-phenyl-1-indenyl)zirconium dichloride (*rac*-Me$_2$Si(2-Me-4-Ph-1-Ind)$_2$ZrCl$_2$). Chemical structures of the catalysts are depicted in figure 4. Both homogeneous[I-IV] and heterogeneous[I-II] versions of the catalysts were studied. The carrier material was silica modified with MAO or TMA.

a) b)

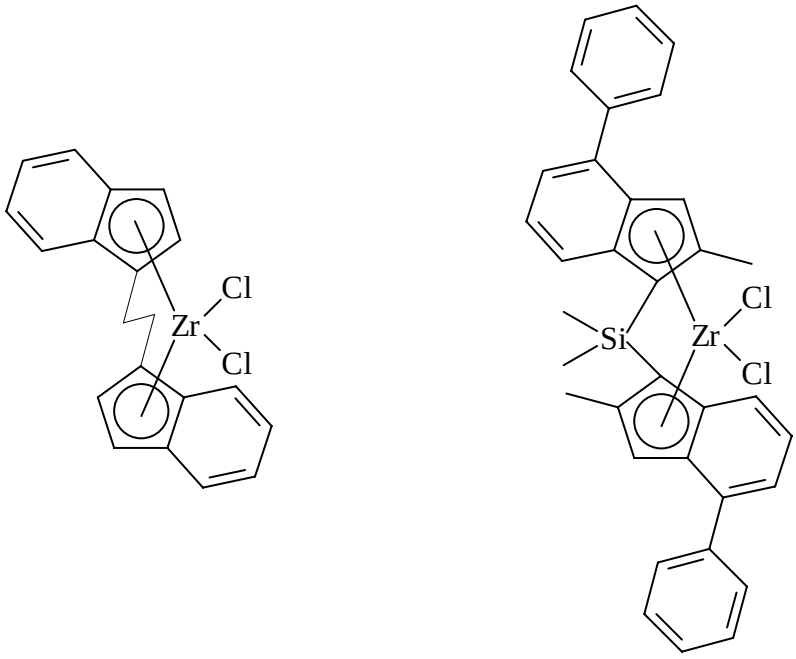

Figure 4. Structures of a) rac-Et(Ind)$_2$ZrCl$_2$ and b) rac-Me$_2$Si(2-Me-4-Ph-1-Ind)$_2$ZrCl$_2$

In preparation of the supported *rac*-Et(Ind)$_2$ZrCl$_2$ catalyst, the silica was partially dehydroxylated by preheating and modified with vaporized TMA before

adsorption of the metallocene. The reaction between the metallocene and TMA was confirmed by the disappearance of the peak corresponding to $–AlCH_3$ groups in the FTIR spectrum.

Impregnation of *rac*-$Et(Ind)_2ZrCl_2$ on the carrier decreased the catalyst activity in propylene polymerization to a fraction of the original. With impregnation of *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$, the activity was still on an adequate level. TIBA was unable to activate the metallocene, and external MAO was required.

8.1 Copolymerization with supported metallocene catalyst

rac-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ supported on MAO-modified silica was tested in the copolymerizations reported in publication **II**. The 2-methyl substitution gave high molecular weight while the 4-aryl substitution lead to good thermal properties and high isotacticity. This applies both to homogeneous and heterogeneous version of the catalyst. 1-Hexene and 1-tetradecene were selected as short and long α-olefin comonomers to induce a small amount of short chain branching in the polypropylene. Symmetric 1,9-decadiene (DD) and sterically hindered 7-methyl-1,6-octadiene (MOD), in turn, were used to obtain long-chain branches. *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ catalyst supported on MAO-modified silica polymerized all four comonomers with propylene. Polymerization results of homopolymerization (PP) and of copolymerization with 7-methyl-1,6-octadiene (PP/MOD), 1,9-decadiene (PP/DD), 1-hexene (PP/Hx), and 1-tetradecene (PP/14C) are presented in Table 1.

Table 1. Polymerization results with supported rac-Me_2Si(2-Me-4-Ph-1-Ind)$_2ZrCl_2$.[a, II]

exp.	n (Zr) μmol	comon. conc. mol/dm^3	polym. time min	activity kg/mol h	T_m °C	ΔH_m kJ/mol	M_w kg/mol	M_w/M_n	[mmmm] %	comon. incorp. mol-%
PP1	1.7	0	30	15 000	156.4	112	122	2.4	94.6	0
PP2	1.0	0	15	53 000	155.4	105	180	2.4	n.d.	0
PP3[c]	2.5[b]	0	30	0[c]	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]
PP/MOD1	6.0	0.014	45	1200	141.8	94	76	2.0	96.6	0.20
PP/MOD2	6.4	0.011	20	5800	151.3	91	68	2.1	96.6	0.10
PP/MOD3	4.0	0.014	20	18 000	154.5	102	83	2.3	93.2	0[d]
PP/DD1	4.6	0.014	10	14 000	139.0	76	544	9.1	93.3	0.64
PP/DD2	1.2	0.028	15	57 000	151.2	100	368	4.8	94.7	0.40
PP/DD3	0.8	0.028	20	54 000	150.7	90	977	12.0	94.5	0.15[e]
PP/Hx1	1.0	0.027	30	31 400	150.7	100	152	2.3	95.4	0.15
PP/Hx2	0.8	0.015	30	19 500	147.0	95	176	2.3	93.5	0.38
PP/14C1	4.0[b]	0.006	30	3900	154.3	100	171	2.4	95.0	0.04
PP/14C2	1.0	0.029	30	46 100	144.9	86	149	2.3	95.1	0.56

[a] Reactor volume 0.5 dm^3, 300 cm^3 *n*-heptane, propylene overpressure 5.0 bar, polymerization temperature 80 °C, Al/Zr ratio 2000 mol/mol; [b] Al/Zr ratio was only 1000 mol/mol; [c] TIBA was used as cocatalyst, but it could not activate the catalyst; [d] No comonomer detected by ^{13}C NMR; [e] Only carbons attached directly to the main chain detected by ^{13}C NMR

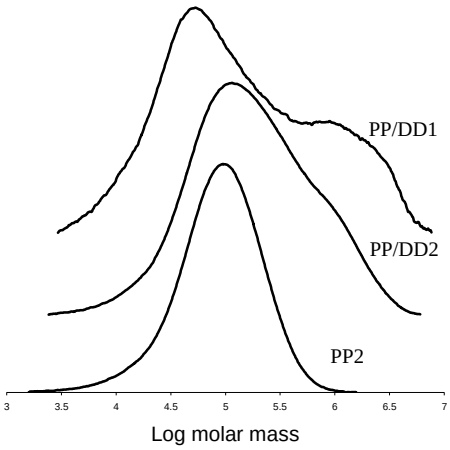

Figure 5. GPC curves with increasing 1,9-decadiene content.[II]

MOD lowered the molecular weight even in low concentration. MOD behaved as a chain transfer agent. DD had the opposite effect: molecular weight was increased and molecular weight distribution was broadened. (Fig. 5)

An example of a PP/DD ^{13}C NMR spectrum is depicted in Figure 6. Carbons corresponding to the peaks are marked in the scheme of the chemical structure. Comonomer contents were determined from the α carbon, branch carbon, and the side chain carbon closest to the main chain. With α-olefins the carbon at the end of the side chain was also visible.

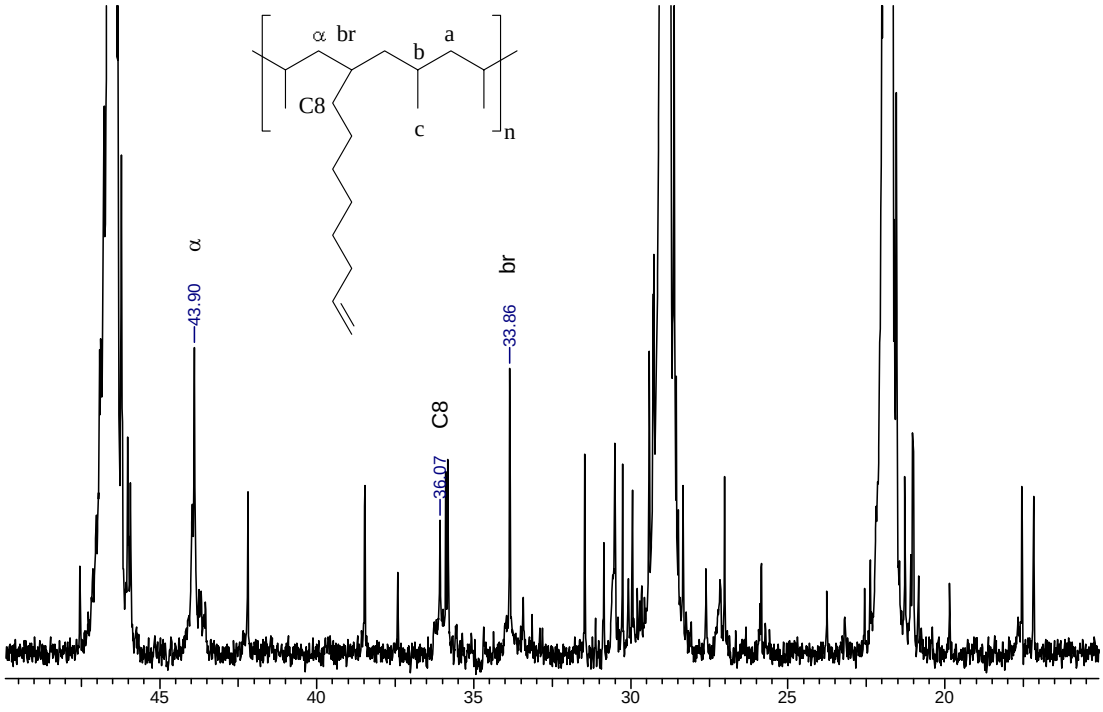

Figure 6. ^{13}C NMR spectrum of 1,9-decadiene/propylene copolymer.[II]

8.2 Dynamic rheological analysis of long-chain branching

PP2, PP/DD1, PP/DD2, PPHx2, and PP/14C1 were selected for dynamic rheological analysis. In addition, polypropylene PP4, which has a molecular weight closer to the molecular weights of the PP/DD copolymers was used as reference. The results obtained with the stress-controlled rheometer are presented in Table 2.

Table 2. Results of dynamic rheological tests.[II]

exp.	M_w kg/mol	M_w/M_n	comon. incorp. mol-%	η_0 extrapolated at 200 °C	E_a kJ/mol	G' at G" (2000) at 200 °C	G' at G" (5000) at 200 °C	G' at G" (10 000) at 200 °C
PP2	180	2.4	0	892	49	350	1460	4160
PP4	387	2.4	0	13 631	44	388	1410	3860
PP/DD1	544	9.1	0.64	80 709	68	2980	7630	15 000
PP/DD2	368	4.8	0.40	39 798	100	1640	4820	10 700
PP/Hx2	176	2.3	0.38	634	39	241	1100	3390
PP/14C1	171	2.4	0.04	847	42	381	1510	4220

Methyl substituent next to the double bond of MOD decreased the reactivity of the double bond and eliminated the possibility of formation of cross-links between the growing polypropylene chains and long-chain branching. Furthermore, the decreasing effect on the molecular weight made it impossible to perform reliable rheological measurements when MOD was involved.

Zero shear viscosities were extrapolated from the complex viscosity curves (Fig. 7). With the PP/DD copolymers, the complex viscosity did not reach a plateau, and this may have created some inaccuracy in the exact values; but the extrapolated zero shear viscosities were on a much higher level than would have been expected from the molecular weights. Arrhenius-type flow activation energies of the PP/DD copolymers

were much higher than those of the reference samples. A still clearer difference was seen in the elasticity index of the materials.

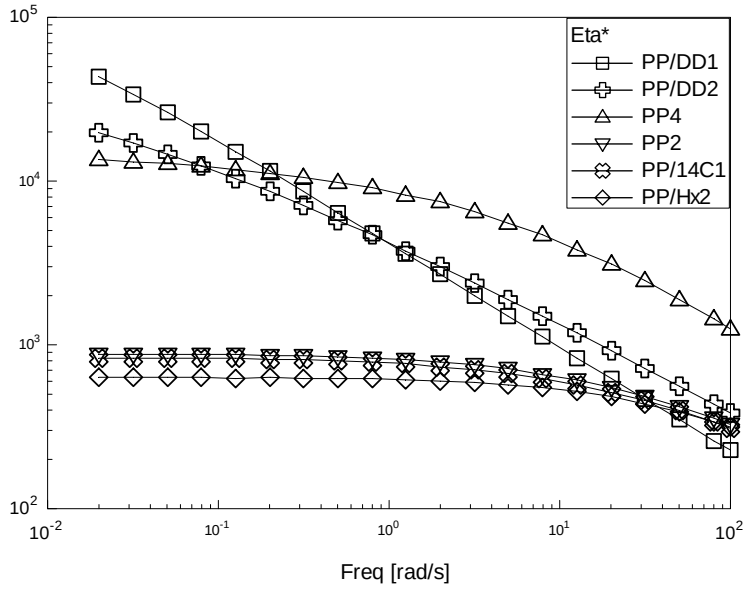

Figure 7. Complex viscosities of the selected samples measured at 200 °C.[II]

The change in rheological behavior is best observed by comparing the samples PP/DD2 (Fig. 8) and PP4 (Fig. 9), which have almost identical molecular weights. The G'-G" moduli crossover occurred at a lower frequency in PP/DD2 and the dynamic moduli G' (△) and G" (□) were linear and almost parallel. Higher elasticity index, elevated zero shear viscosity, increased shear thinning, changed rheological behavior, and especially raised Arrhenius-type flow activation energies indicated long-chain branching in propylene/1,9-decadiene copolymers.

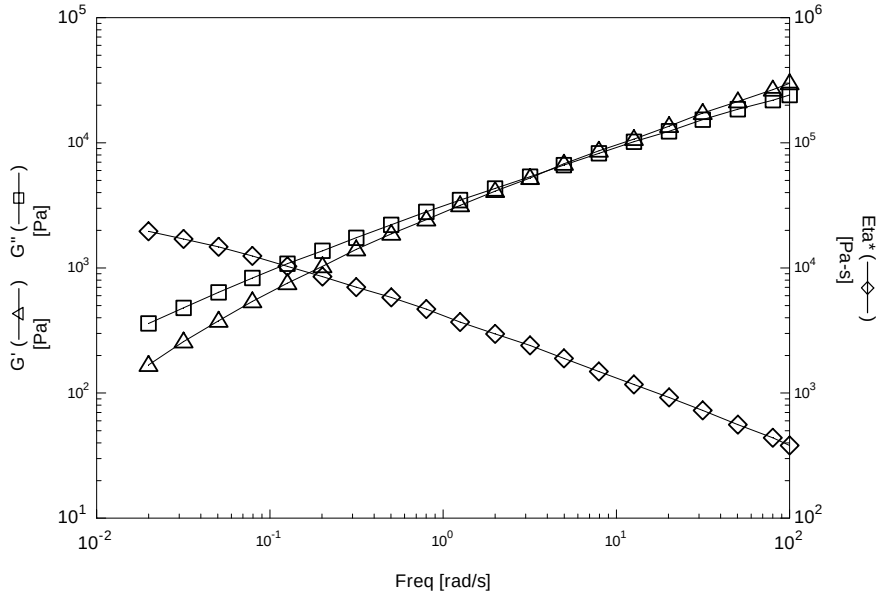

Figure 8. Frequency sweep of PP/DD2 at 200 °C showing long-chain branching.[II]

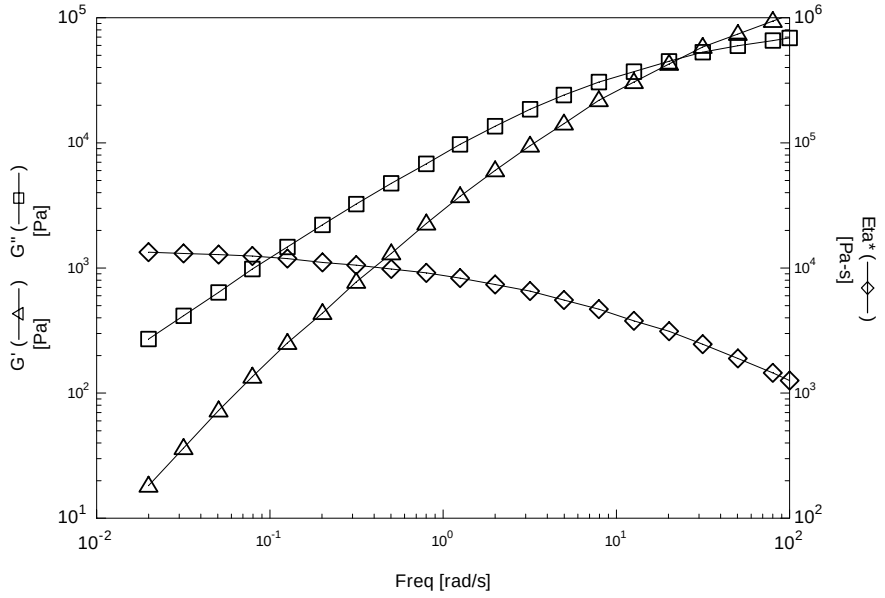

Figure 9. Frequency sweep of the reference homopolypropylene PP4 at 200 °C.[II]

8.3 Polymerization of hydroxyl functional polypropylene

Homogeneous *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ was used to copolymerize propylene and 10-undecen-1-ol, as reported in publications **III-IV**. Typical ways to minimize catalyst deactivation are to insert a spacer between the reactive double bond and the functional group or steric hindrance around the functional group. Because we wished to maximize the adhesion properties of the functional polypropylene, the idea of shielding was discarded and a straight long-chain alcohol with a spacer of nine carbons and without any bulky substituents was selected as the comonomer. To prevent catalyst deactivation a large amount of aluminum alkyl compound was needed for complex formation with the alcohol comonomer. The typical aluminum/comonomer ratio was about 6. Ash content measurements were performed to confirm the complete removal of aluminum from the samples used in the adhesion tests. Two copolymerization series were run, with different cocatalysts: in the first MAO (M) and in the second a mixture of MAO and TIBA (T). In the latter, the concentration of MAO was kept constant (10 mmol/L) independent of the amount of the comonomer, and the concentration of TIBA was varied (8-140 mmol/L). In a further series, also the MAO concentration was adjusted. The most relevant polymerization results are presented in Table 3.

The catalyst system was extremely sensitive to the aluminum/comonomer ratio. When the ratio was decreased from 6 to 4, less than 5% of the polymerization activity was retained. In comparison of experiments M2 and M4, increase in concentration of the polar comonomer causes the polymerization activity to drop drastically.

Table 3. Polymerization results for hydroxyl functional polypropylene.[a, III]

run	comon. conc.[b]	MAO[b]	TIBA[b]	n (Zr) μmol	Al//Zr (MAO)	yield g	activity[c]	T_m °C	ΔH_m kJ/mol	M_w kg/mol	M_w/M_n	comon. incorp.[d]
PP1	0	10	0	0.2	15 000	13.3	133 000	152.7	112	80	1.9	0/0
M1	3	18	0	1.5	3600	4.3	5700	149.7	114	74	2.0	0.2/0.7
M2	10	60	0	1.5	12 000	8.2	11 000	145.4	101	46	2.0	0.6/2.3
M3	15	90	0	1.7	16 000	17.6	21 000	144.7	105	37	1.9	0.6/2.3
M4[e]	15	60	0	1.7	10 600	0.6	700	138.2	84	44	1.8	2.1/8.6
T1	3	10	8	1.2	2500	12.0	20 000	151.4	93	99	2.0	0.1/0.5
T2	10	10	50	0.4	7500	7.8	39 000	148.3	87	107	1.9	0.3/1.3
T3	15	10	80	1.0	3000	15.1	30 000	146.7	91	105	2.0	0.4/1.7
T4	20	10	110	1.5	2000	14.1	19 000	149.0	70	92	1.9	0.6/2.3
T5[f]	30	10	140	1.6	1900	8.8	11 000	142.0	65	99	1.9	0.9/3.6

[a] Reactor volume 0.5 L, 300 mL toluene, propylene overpressure 3.0 bar, polymerization temperature 80 °C, polymerization time 30 minutes, stirring speed 500 rpm, aluminum/comonomer ratio 6; [b] Concentration in mmol/L; [c] Activity measured as $kg_{PP}/(mol_{Zr} * h)$; [d] mol %/wt %; [e] Aluminum/comonomer ratio 4; [f] Aluminum/comonomer ratio 5.

Since TIBA could not activate the metallocene by itself, the aluminum in TIBA was ignored and only aluminum in MAO was considered in calculating the Al/Zr ratio,. Polymerization activity decreased steadily as the Al/Zr ratio was decreased from 7500 to 3000, 2000, and 1900 mol/mol. Polymerization activity was more stable with the combination of MAO and TIBA, probably because interactions between the active center and the polar end group of the comonomer were more efficiently blocked. The molecular weight drop caused by the TMA present in MAO was eliminated with the addition of TIBA.

An example of the ^{1}H NMR spectrum of the propylene-*co*-10-undecen-1-ol copolymer is depicted in Figure 10. The two hydrogens attached to the carbon next to hydroxyl give a clear triplet at δ 3.55-3.60 ppm, which was used in determining the comonomer incorporations. An example of the ^{13}C NMR spectrum of the propylene-*co*-

10-undecen-1-ol copolymer with highest comonomer content is depicted in Figure 11. The α carbon, branch carbon, and side chain carbons are visible in the spectrum. The resonance at δ 125-138 ppm is due to the solvent trichlorobenzene.

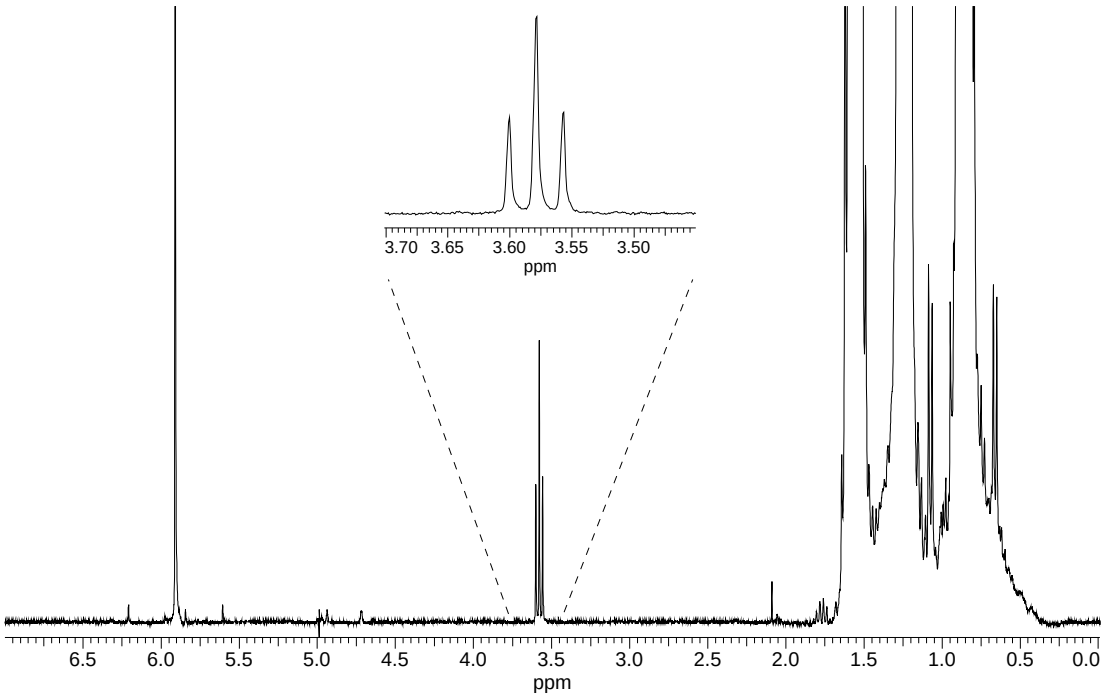

Figure 10. ^{1}H NMR spectrum of 10-undecen-1-ol/propylene copolymer.[III]

With MAO, comonomer incorporations of 0.6 mol %/2.3 wt % were achieved, but then remained at that level even when the concentration of the comonomer in the feed was increased. As can be seen from Figure 12, the comonomer was less reactive with the combination of MAO and TIBA, but higher concentrations of comonomer could then be used in the feed and comonomer incorporations as high as 0.9 mol %/3.6 wt % were achieved.

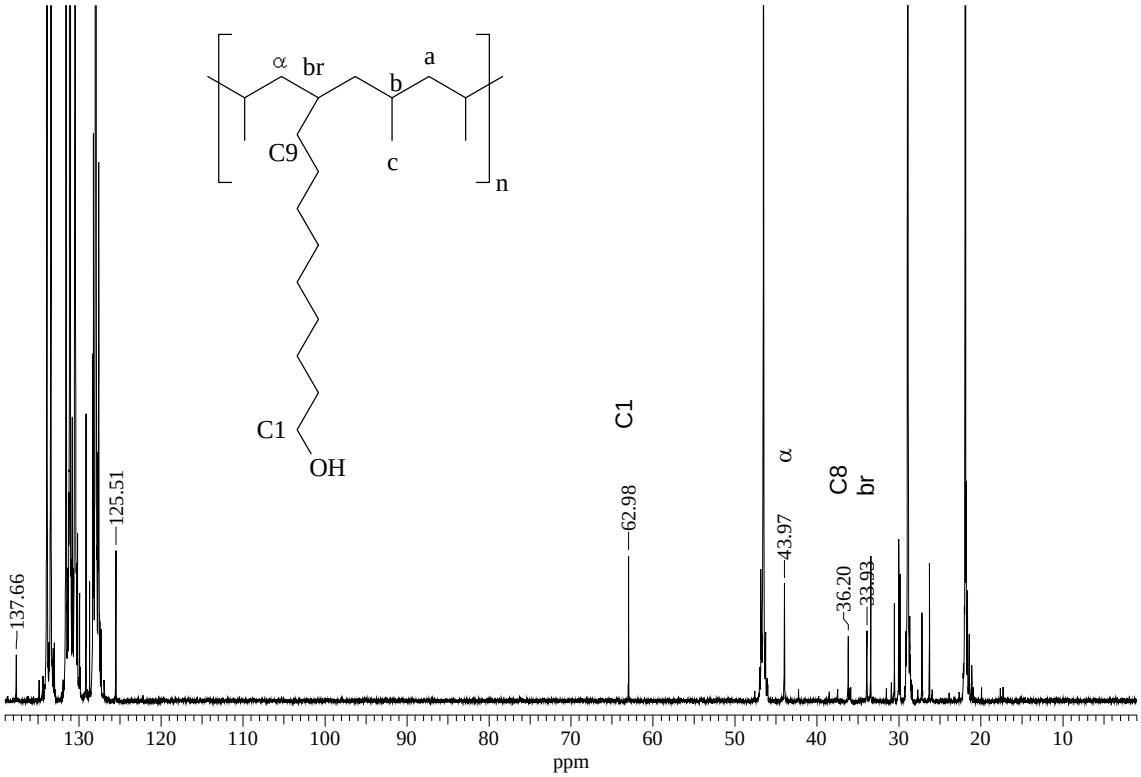

Figure 11. ^{13}C NMR spectrum of 10-undecen-1-ol/propylene copolymer.[IV]

A mixture of MAO and TIBA was also used as cocatalyst in the polymerization series reported in publication **IV**. Pressure and MAO concentration, earlier kept constant, were now adjusted. Increase in concentration of MAO, aluminum/comonomer ratio, and pressure all enhanced polymerization activity. When MAO concentration was doubled from 10 mmol/L to 20 mmol/L, activity increased more than twofold. Reasonable activities could be achieved by keeping the MAO/Zr ratio above 2000, and the activity was by no means limited by high comonomer concentration. Increase in pressure from 1 bar to 2 bar increased polymerization activity by 70 %. When the pressure was further elevated to 3 bar, the activity increased still 30 % over the level at 2 bar. Polypropylene with molecular weight of 104 kg/mol and comonomer incorporation of 0.9 mol % was obtained with relatively high activity of

27 300 $kg_{PP}/(mol_{Zr} \times h)$ when concentration of MAO was 20 mmol/L, aluminum/comonomer ratio 4 and MAO/Zr ratio 10 000. Polymerization pressure was 2 bar and temperature 70 °C.

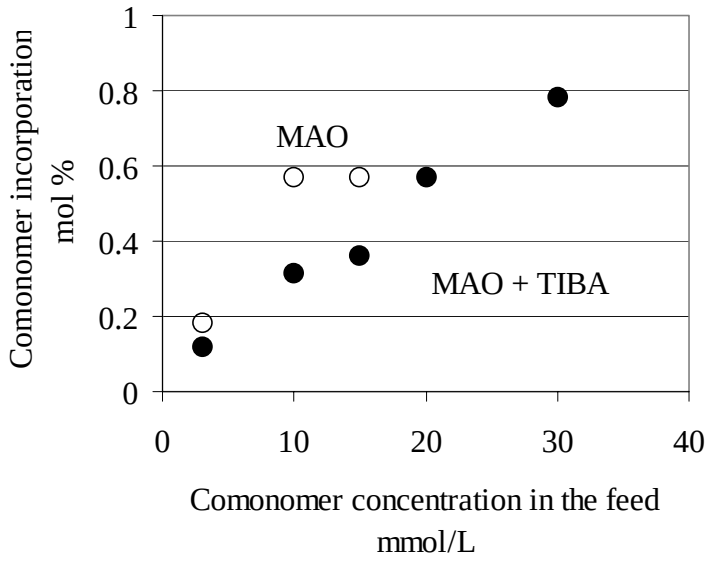

Figure 12. Effect on the incorporation of 10-undecen-1-ol of using MAO alone (○) and a combination of TIBA and MAO (●) as cocatalyst.[III]

The effect of pressure on molecular weight and comonomer incorporation is depicted in Figure 13. At lower pressure, comonomer incorporations up to 2 mol % could be obtained. Pressure increase from 1 bar to 2 bar and further to 3 bar caused the incorporation to decrease from 2 mol % to 0.9 mol % and further to just traces of comonomer. In contrast, the molecular weight increased from 53 kg/mol to 104 kg/mol and further to 132 kg/mol almost linearly with propylene pressure. The propylene concentration in toluene was higher at elevated pressure leading to higher molecular weight; at the same time the comonomer had to compete harder with propylene monomer to gain access to the growing polymer chain.

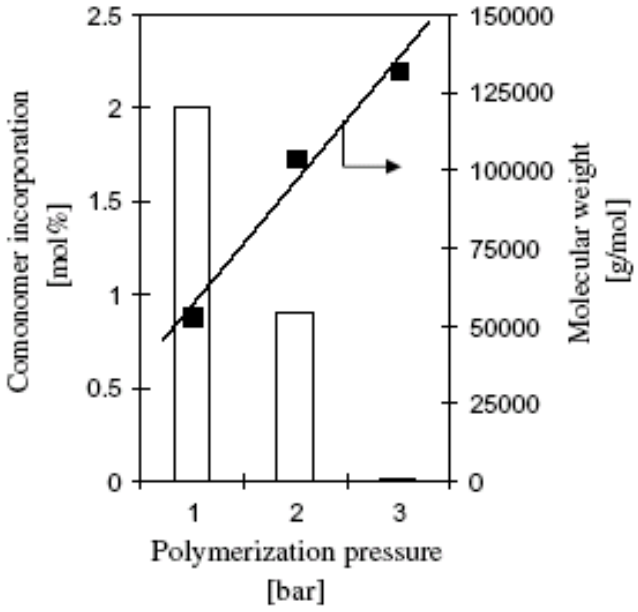

Figure 13. Dependence of comonomer incorporation (columns) and molecular weight (symbols ■) on polymerization pressure.[IV]

To conclude, a successful polymerization depends on a delicate balance among polymerization activity, molecular weight, and functionality content. Polymerization activity has to be reasonably high in order to obtain some polymer product, and this requires that the aluminum to comonomer ratio be above a critical level of four. The same applies to the ratio of MAO to zirconium which has to be kept above 2000 mol/mol. Too low polymerization pressure reduces activity. Polypropylene with functionality content of 0.3-1.0 mol % and with molecular weight of 90-110 kg/mol was obtained at 2 bar with activity of 30 000-40 000 $kg_{PP}/(mol_{Zr} * h)$. When pressure was increased from 2 bar to 3 bar in order to enchance activity and molecular weight, the functionality content rapidly dropped to just traces of comonomer. Sufficiently high molecular weight is required for technical applications and this requires low

temperature even in the presence of TIBA. However, at low polymerization temperatures, if the TIBA concentration and especially the MAO concentration are at the desired high level, the aluminum alkyls may form a gel-like network with toluene. Apart from the providing of a major portion of the aluminum alkyl as MAO rather than TIBA, all these improvements in the polymerization conditions are done at the expense of the desired high functionality content. When pressure was lowered from 2 bar to 1 bar in order to obtain higher functionality contents of 2.0 mol %, activity decreased to 16 000 $kg_{PP}/(mol_{Zr} * h)$ and molecular weight to 53 kg/mol.

8.4 Surface adhesion properties of functional polypropylene

Typically 1-20 mol % (3-40 wt %) grafted functional polypropylene has been used in polymer blends to obtain improvements in the adhesion or compatibility. If the amount of compatibilizer could be decreased, the effect on the properties of polypropylene and especially on the impact strength would be minimal. When the properties of the matrix dominate in the blend, they can be varied simply by selecting suitable matrix from the wide range of polypropylenes.

The adhesion properties of a polypropylene with functionality content of 0.4 mol % (1.7 wt %) were compared to commercial polypropylene homopolymer (PP), acrylic acid grafted (PP-g-AA), and maleic anhydride grafted polypropylene (PP-g-MAH). The results are reported in publication **III**.

Figure 14 shows the relationship between peel strength and contact angle for the tested materials. As can be seen, these properties are inversely proportional to each other, and all the polar materials have good peel strengths and lower contact angles than the polypropylene homopolymer. Adhesion to aluminum was non-existent for

polypropylene homopolymer, but it was significantly improved when hydroxyl functional polypropylene was blended into the homopolymer. The paintability was also improved. Hydroxyl functional polypropylene improves the adhesion properties also as an additive, and at functionality contents as low as 0.2 mol % (0.17 wt %).

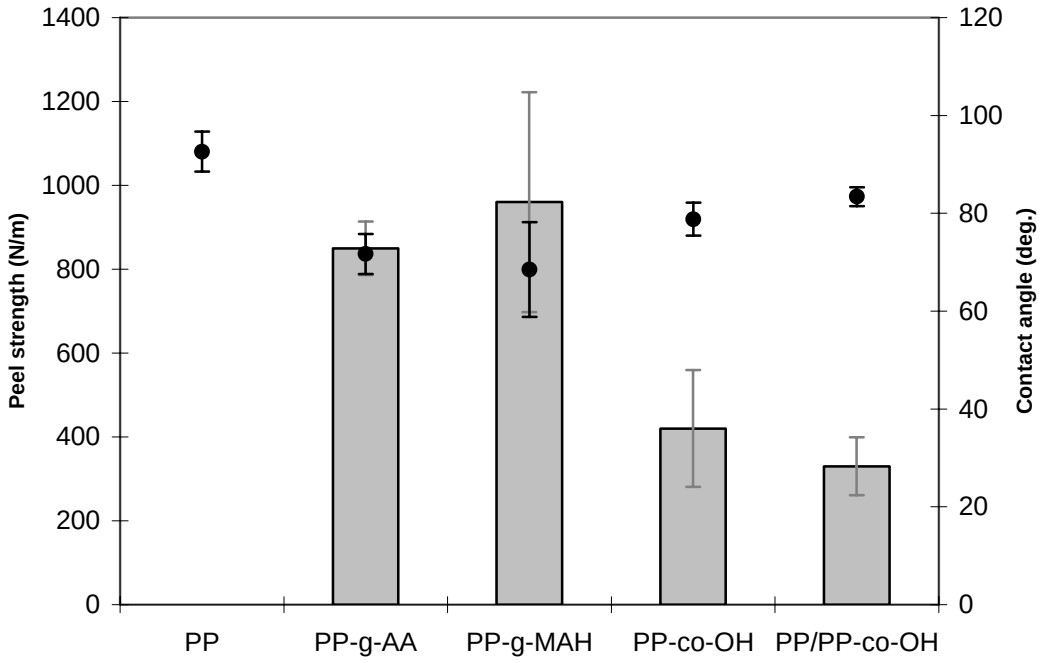

Figure 14. Peel strength (columns) and contact angle (symbols) for functional PPs.[III]

8.5 Functional polypropylene as compatibilizer in PP/PA blend

The main goal in blending polymers is to combine the good properties of the two components. This is not possible, however, without a compatibilizer to link the components together. The adhesion between the polymer phases has to be strengthened, and a functional polypropylene is suitable for the purpose. In PP/PA blend, the

polypropylene backbone penetrates the polyolefinic phase, and functional hydroxyl groups interact with the polar polyamide phase.

Hydroxyl functional polypropylenes T1, T4, and T5 were tested as compatibilizers in polypropylene/polyamide 6 blends.[V] The synthesis and properties of these polypropylenes have been described above (see Table 3). One additional hydroxyl functional polypropylene was tested and marked with T*. The blend composition was PP/PA6 (70/30). The amount of the compatibilizer was 10 wt % and this was subtracted from the polypropylene phase. Commercial maleic anhydride grafted polypropylene (PP-g-MAH) was tested for comparison.

Addition of the functional copolymer did not change the ellipsoidal form of the polyamide particles or decrease the particle size in the blend when the functionality content of the compatibilizer was 0.4 mol % or lower. When the content was increased closer to that of the commercial compatibilizer, all the particles appeared to be rounded, but unlike with PP-*g*-MAH the particle size was still on the same level as in the binary blend.

The mechanical properties of the blends compatibilized with functional copolymers are presented in Table 4. The impact strength was in all cases relatively poor. However, the copolymer with functionality content of 0.1 mol % improved the elongation at break, which indicates that low hydroxyl functionality content may be sufficient to improve the adhesion between the polypropylene and polyamide phases. Compatibilizer with functionality content of 0.6 mol % or higher had no effect. Higher functionality content makes it more difficult for the compatibilizer to penetrate the polypropylene phase.[92]

Table 4. Mechanical properties of PP/PA6 blends.[V]

	Tensile modulus E MPa	Tensile strength σ MPa	Elongation at break ε_b %	Charpy impact strength	
				notched	unnotched
PP	605 (17)	29.9 (1.3)	> 500	2.2 (0.1)	9.8 (3.6)
PA6	1049 (29)	64.8 (2.0)	357 (11)	5.3 (0.5)	NB
PP/PA6	877 (12)	37.9 (0.3)	15.7 (0.9)	2.2 (0.2)	15.2 (1.4)
+PP-g-MAH	900 (28)	38.7 (1.3)	15.5 (1.7)	2.0 (0.2)	26.5 (4.7)
+T1/0.1 mol %	929 (35)	38.6 (1.4)	53.6 (9.4)	1.7 (0.3)	12.6 (2.6)
+T*/0.4 mol %	886 (32)	38.2 (0.6)	16.4 (1.5)	1.7 (0.2)	12.6 (2.1)
+T4/0.6 mol %	778 (51)	35.9 (3.5)	12.7 (1.6)	1.5 (0.3)	
+T5/0.9 mol %	745 (17)	30.4 (1.0)	12.9 (1.3)	1.4 (0.1)	

Standard deviation in parentheses

These results were supported by dynamic mechanical analysis. In addition, decreased damping indicated improved interfacial adhesion, although it was more pronounced with PP-*g*-MAH than with metallocene-catalyzed functional copolymers.

8.6 Adhesion promoter in polypropylene/silica composite

Silica is used as a filler in polypropylene to improve the stiffness of polypropylene casings. Without good adhesion between the filler particles and polypropylene phase, the separate particles serve as start points for cracks. Compatibilizer improves adhesion in composites similar to blends: the polypropylene backbone penetrates the polyolefinic phase, and functional hydroxyl groups interact with the polar silica particles.

The functional polypropylene was tested as an adhesion promoter in polypropylene/organoclay composite.[VI] The nanoscale montmorillonite was organomodified with *N*-methyl-10-undecenylamine before the preparation of

nanocomposite. An amount of adhesion promoter equal to the amount of modified organoclay did not significantly increase the distance between the silica layers. At higher nano filler contents the nano particles may start to agglomerate if the amount of compatibilizer is not sufficient to distribute the filler uniformly into the polypropylene matrix. According to the small angle X-ray scattering and SEM analyses, exfoliated structure was obtained when the amount of adhesion promoter was double the amount of modified organoclay. Then the amount of functional polypropylene was sufficient for it to penetrate the galleries of the organoclay instead of simply wrapping around the clay particles. The metallocene-catalyzed functional polypropylene was almost as efficient an adhesion promoter as PP-*g*-MAH.

The functional polypropylene was also tested as an adhesion promoter in a polypropylene/polymer grade microsilica composite.[VII] The interactions between the hydroxyl groups of the functional polypropylene and the hydroxyl groups on the microsilica surface altered the crystallization process and improved the nucleating activity of the microsilica because the filler particles, which serve as nucleation centers, were uniformly dispersed within the polypropylene matrix. However, the metallocene-catalyzed functional polypropylene did not improve either impact strength or elongation at break. The miscibility with the polypropylene matrix may have been hindered by the uniformly distributed hydroxyl groups or by the differences in molecular weight and molecular weight distribution of the functional polypropylene and matrix.

9 CONCLUSIONS

Industrial use of metallocene catalysts requires heterogenization of the catalyst. It then has to be ensured that the catalyst is stable, polymerization activity is on a satisfactory level, no leaching occurs from the support surface, and the stereospecificity of the catalyst is maintained.

Propylene can be polymerized under both homogeneous and heterogeneous conditions with racemic ethylene*bis*(1-indenyl)zirconium dichloride and racemic dimethylsilanyl*bis*(2-methyl-4-phenyl-1-indenyl)zirconium dichloride.

Methylaluminoxane-activated *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ supported on MAO-modified silica copolymerized propylene with 1,9-decadiene. Although comonomer incorporations were less than 1 mol %, they had a significant effect on the rheological properties of polypropylene. Molecular weight was increased and molecular weight distribution was broadened as the diene connected two growing polypropylene chains. Higher elasticity index, elevated zero shear viscosity, increased shear thinning, changed rheological behavior, and especially raised Arrhenius-type flow activation energies indicated long-chain branching in propylene/1,9-decadiene copolymers. Long-chain branching improves the processability of the isotactic polypropylene produced by metallocene catalyst.

Homogeneous *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$ activated with MAO or with MAO and TIBA copolymerized propylene with 10-undecen-1-ol. Comonomer incorporations were 0.1-2.0 mol % but had a significant effect on the adhesion properties of polypropylene. With a combination of MAO and TIBA as cocatalyst instead of MAO alone, the catalyst deactivation was diminished, because interactions between the active center and the hydroxyl group at the end of the comonomer chain

were more effectively blocked. Also, the decrease in molecular weight associated with the increase in MAO concentration with increasing comonomer concentration was eliminated with the addition of TIBA. As a disadvantage, the comonomer reactivity was slightly reduced.

The polymerization activity could be enhanced by adjusting the proportion of MAO in the mixture of MAO and TIBA used as cocatalyst. Further increase in comonomer incorporation was accomplished at the expense of molecular weight and activity by decreasing the propylene concentration, i.e. polymerization pressure. Hence, a compromise among polymerization activity, functionality content and molecular weight must be sought in order to obtain functional polypropylene with optimal properties for particular technical applications.

The functional polypropylene exhibited significantly enhanced peel strength and paintability relative to a reference homopolypropylene. Smaller contact angles provided further evidence of a changed surface polarity. Furthermore, adhesion properties were improved not only in the copolymer but also in a blend consisting of homopolypropylene and functional polypropylene, even though functionality content was only 0.17 wt %.

The composites and blends were more difficult to prepare than expected. Despite the hazards of volatile maleic acid anhydride and the random comonomer distribution obtained in graft reactions, the higher reactivity of this functional group might still favor PP-*g*-MAH over more environmentally friendly solutions. Although the adhesion between polypropylene and polyamide phase or silica fillers was somewhat improved with metallocene-catalyzed functional polypropylene as compatibilizer, the impact strength was fairly poor. The narrow molecular weight distribution and uniform

comonomer distribution associated with metallocene catalysts might turn out to be an Achilles heel if they hinder the miscibility of functional polypropylene into the propylene matrix. Surprisingly, best results were obtained with lowest functionality content.

With metallocene catalysts the comonomer distribution is uniform along the polypropylene backbone and the comonomer does not disturb the organized stereostructure of the polypropylene. The properties of polypropylene are dramatically affected even with very low comonomer incorporations when these are evenly distributed, regardless of whether the comonomer contains several reactive double bonds to induce long-chain branching or a functional group to improve adhesion properties.

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